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Oil Baths

Field of the invention

This invention relates to clear, alkanolamide- and water-free cosmetic preparations for use in skin and hair care with a defined content of a mixture of fatty alcohol (polyglycol) esters, fatty alcohol polyglycol ethers, polyols, alkyl and/or alkenyl oligoglycosides and oil components.

Prior art

For the production of cosmetic preparations, surfactants and oils may be mixed with one another in any ratio according to the application envisaged. Hitherto, the corresponding formulations have contained alkanolamides which belong to the "nitrosamine-forming substances". Nitrosamines can have a harmful effect in any quantity, however small, not only through their presence in cosmetics, but also if they enter the body. For this reason, cosmetic preparations with no alkanolamides are desirable. By contrast, the removal of alkanolamides from the surfactant mixtures leads to cloudy formulations on mixing with oil components.

Accordingly, the problem addressed by the present invention was to provide clear, water-free cosmetic preparations which would not turn cloudy, even in storage, by mixing alkanolamide-free surfactant mixtures with defined quantities of oil components.

Description of the invention

The present invention relates to alkanolamide-free cosmetic preparations consisting of

- (a) 30 to 70% by weight of a mixture of (a1) fatty acid (polyglycol) esters, (a2) fatty alcohol polyglycol ethers, (a4) alkyl and/or alkenyl oligoglycosides and/or (a3) polyols and

- A2 (b) 70 to 30% by weight of oil components,
with the proviso that the quantities add up to 100% by weight.

The present invention also relates to the use of these mixtures for the production of clear, alkanolamine-free cosmetic preparations.

- 5 It has surprisingly been found that clear water-free cosmetic preparations can be obtained from cloudy, alkanolamide-free surfactant mixtures consisting of fatty acid (polyglycol) esters, fatty alcohol polyglycol ethers, polyols, alkyl and/or alkenyl oligoglycosides by adding a defined quantity of oil components. These cosmetic preparations are additionally
10 distinguished by good refatting, good foam properties and stability in storage.

Fatty acid (polyglycol) esters

- The preparations according to the invention may contain fatty acid
15 (polyglycol) esters - component (a1) - which correspond to formula (I):



(I)

- 20 where R^1CO is a linear or branched, saturated or unsaturated acyl group containing 6 to 30, preferably 8 to 22 and more particularly 10 to 18 carbon atoms, x has an average value of 0 to 30, preferably 5 to 20 and more particularly 10 to 15 and AO is a CH_2CH_2O -, $CH_2CH(CH_3)O$ - and/or $CH(CH_3)CH_2O$ group and R^2 is a linear or branched, saturated or
25 unsaturated alkyl group containing 1 to 4 and preferably 1 and/or 2 carbon atoms, more particularly methyl,
and which are produced by esterification of the corresponding fatty acid (polyglycols) which, in turn, are obtainable by the relevant preparative methods of organic chemistry. To this end, ethylene oxide, propylene
30 oxide or a mixture thereof is optionally added - in random or block distribution - onto the corresponding fatty acids in the presence of an acid

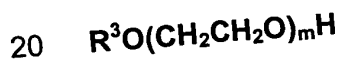
as catalyst, but preferably in the presence of bases, for example sodium methyrate or calcined hydrotalcite. Typical examples of suitable starting materials are the addition products of 10 to 15 moles of ethylene oxide and/or propylene oxide, but preferably the addition products of 12 moles of ethylene oxide or 12 moles of propylene oxide with caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof, which are then esterified. The fatty acid (polyglycol) esters may be used in the process according to the invention in quantities of 0.1 to 20% by weight, preferably in quantities of 0.5 to 10% by weight and more particularly in quantities of 1 to 5% by weight, based on the keratin-reducing substance or the oxidizing agent.

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Fatty alcohol polyglycol ethers

Fatty alcohol polyglycol ethers which form component (a2) are primary aliphatic polyglycol ethers corresponding to formula (II):

(II)



in which R^3 is a linear or branched, saturated or unsaturated C_{10-18} hydrocarbon radical and m is a number of on average 2 to 6. Typical examples are products of the addition of on average 2 to 6 moles of ethylene oxide onto lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroseliny alcohol, linolyl alcohol, linolenyl alcohol and elaeostearyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as

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monomer fraction in the dimerization of unsaturated fatty alcohols. Ethoxylates of technical C₁₂₋₁₄ fatty alcohols, for example coconut or palm kernel fatty alcohol, are preferred.

5 **Polyols**

Polyols which form component (a3) preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. The polyols may contain other functional groups, more especially amino groups, or may be modified with nitrogen. Typical examples are

- 10 ➤ glycerol;
- alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols with an average molecular weight of 100 to 1000 dalton;
- 15 ➤ technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- 20 ➤ lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms in the alkyl group, for example methyl and butyl glucoside;
- sugar alcohols containing 5 to 12 carbon atoms, for example sorbitol or mannitol,
- sugars containing 5 to 12 carbon atoms, for example glucose or
- 25 sucrose;
- amino sugars, for example glucamine;
- dialcoholamines, such as diethanolamine or 2-aminopropane-1,3-diol. Glycerol, butylene glycol, hexylene glycol, polyethylene glycols and, more particularly, propylene glycol with an average molecular weight of 100 to
- 30 1,000 dalton are preferably used.

The preparations according to the invention may contain components (a) in quantities of 30 to 70% by weight, preferably 40 to 60% by weight and more particularly 50% by weight. In a preferred embodiment of the invention, the preparations contain a mixture of (a1) fatty acid (polyglycol) esters, preferably 45% by weight, (a2) fatty alcohol polyglycol ethers, preferably 45% by weight, and (a3) polyols, preferably 10% by weight.

Alkyl and/or alkenyl oligoglycosides

Alkyl and/or alkenyl oligoglycosides which form component (a4) are known nonionic surfactants which correspond to formula (III):



(III)

where R^4 is an alkyl and/or alkenyl group containing 4 to 22 carbon atoms, G is a sugar unit containing 5 or 6 carbon atoms and p is a number of 1 to 10. They may be obtained by the relevant methods of preparative organic chemistry. The overviews presented by Bierman et al. in **Starch/Stärke** 45, 281 (1993), by B. Salka in **Cosm. Toil.** 108, 89 (1993) and by J. Kahre in **SÖFW-Journal** No. 8, 598 (1995) are cited as representative of the extensive literature available on this subject.

The alkyl and/or alkenyl oligoglycosides may be derived from aldoses or ketoses containing 5 or 6 carbon atoms, preferably glucose. Accordingly, the preferred alkyl and/or alkenyl oligoglycosides are alkyl and/or alkenyl oligoglucosides. The index p in general formula (III) indicates the degree of oligomerization (DP), i.e. the distribution of mono- and oligoglycosides, and is a number of 1 to 10. Whereas p in a given compound must always be an integer and, above all, may assume a value of 1 to 6, the value p for a certain alkyl oligoglycoside is an analytically determined calculated quantity which is generally a broken number. Alkyl

and/or alkenyl oligoglycosides having an average degree of oligomerization p of 1.1 to 3.0 are preferably used. Alkyl and/or alkenyl oligoglycosides having a degree of oligomerization of less than 1.7 and, more particularly, between 1.2 and 1.4 are preferred from the applicational point of view. The alkyl or alkenyl radical R^4 may be derived from primary alcohols containing 4 to 11 and preferably 8 to 10 carbon atoms. Typical examples are butanol, caproic alcohol, caprylic alcohol, capric alcohol and undecyl alcohol and the technical mixtures thereof obtained, for example, in the hydrogenation of technical fatty acid methyl esters or in the hydrogenation of aldehydes from Roelen's oxosynthesis. Alkyl oligoglucosides having a chain length of C_8 to C_{10} ($DP = 1$ to 3), which are obtained as first runnings in the separation of technical C_{8-18} coconut oil fatty alcohol by distillation and which may contain less than 6% by weight of C_{12} alcohol as an impurity, and also alkyl oligoglucosides based on technical $C_{9/11}$ oxoalcohols ($DP = 1$ to 3) are preferred. In addition, the alkyl or alkenyl radical R^4 may also be derived from primary alcohols containing 12 to 22 and preferably 12 to 14 carbon atoms. Typical examples are lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol, brassidyl alcohol and technical mixtures thereof which may be obtained as described above. Alkyl oligoglucosides based on hydrogenated $C_{12/14}$ coconut oil fatty alcohol having a DP of 1 to 3 are preferred.

25 Oil components

Suitable oil components which form component (b) are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms, esters of linear C_{6-22} fatty acids with linear C_{6-22} fatty alcohols, esters of branched C_{6-13} carboxylic acids with linear C_{6-22} fatty alcohols, esters of linear C_{6-22} fatty acids with branched alcohols,

more particularly 2-ethyl hexanol, esters of hydroxycarboxylic acids with linear or branched C₆₋₂₂ fatty alcohols, more particularly dioctyl malate, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, triglycerides based on C₆₋₁₀ fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆₋₁₈ fatty acids, esters of C₆₋₂₂ fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, esters of C₂₋₁₂ dicarboxylic acids with linear or branched alcohols containing 1 to 22 carbon atoms or polyols containing 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C₆₋₂₂ fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C₆₋₂₂ alcohols (for example Finsolv® TN), linear or branched, symmetrical or nonsymmetrical dialkyl ethers containing 6 to 22 carbon atoms per alkyl group, ring opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons. The preparations according to the invention may contain the oil components, preferably castor oil, in quantities of 70 to 30, preferably 60 to 40 and more particularly 50% by weight.

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Commercial applications

The cosmetic preparations according to the invention may be used for the production of clear, alkanolamine-free hair and skin care preparations. The preparations such as, for example, hair shampoos, hair lotions, foam baths, shower baths, creams, gels, lotions, alcoholic and aqueous/alcoholic solutions or emulsions, may contain mild surfactants, emulsifiers, superfatting agents, pearlizing waxes, consistency factors, thickeners, polymers, silicone compounds, fats, waxes, stabilizers, biogenic agents, deodorizing agents, anti-dandruff agents, film-formers, swelling agents, UV protection factors, antioxidants, preservatives, insect

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repellents, self-tanning agents, solubilizers, perfume oils, dyes, germ inhibitors and the like as further auxiliaries and additives.

Typical examples of suitable mild, i.e. dermatologically compatible, **surfactants** are monoglyceride sulfates, mono- and/or dialkylsulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, ether carboxylic acids, α -olefin sulfonates, fatty acid glucamides, alkyl amidobetaines and/or protein fatty acid condensates (preferably based on wheat proteins).

Suitable **emulsifiers** are, for example, nonionic surfactants from at least one of the following groups:

- (1) products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group;
- (2) $C_{12/18}$ fatty acid monoesters and diesters of addition products of 1 to 30 moles of ethylene oxide onto glycerol;
- (3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide adducts thereof;
- (4) products of the addition of 15 to 60 moles of ethylene oxide onto castor oil and/or hydrogenated castor oil;
- (5) polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate isostearate. Mixtures of compounds from several of these classes are also suitable;
- (6) products of the addition of 2 to 15 moles of ethylene oxide onto castor oil and/or hydrogenated castor oil;
- (7) partial esters based on linear, branched, unsaturated or saturated $C_{6/22}$ fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar

alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);

- 5 (8) mono-, di- and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;
- (9) wool wax alcohols;
- (10) polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;
- 10 (11) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol according to **DE 11 65 574 PS** and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol;
- (12) polyalkylene glycols and
- (13) glycerol carbonate.

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Products of the addition of ethylene oxide and/or propylene oxide onto fatty acids, alkylphenols, glycerol monoesters and diesters and sorbitan monoesters and diesters of fatty acids or onto castor oil are known commercially available products. They are homolog mixtures of which the
20 average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C_{12/18} fatty acid monoesters and diesters of adducts of ethylene oxide with glycerol are known as refatting agents for cosmetic preparations from **DE 20 24 051 PS**.

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In addition, zwitterionic surfactants may be used as emulsifiers. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic
30 surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycines, for example cocoalkyl dimethyl ammonium

glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocoamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8/18} alkyl or acyl group, contain at least one free amino group and at least one -COOH- or -SO₃H- group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and C_{12/18} acyl sarcosine. Besides ampholytic emulsifiers, quaternary emulsifiers may also be used, those of the esterquat type, preferably methyl-quaternized difatty acid triethanolamine ester salts, being particularly preferred.

Superfatting agents may be selected from such substances as, for example, lanolin and lecithin and also polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the fatty acid alkanolamides also serving as foam stabilizers.

Suitable **pearlizing waxes** are, for example, alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms,

especially long-chain esters of tartaric acid; fatty compounds, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain in all at least 24 carbon atoms, especially laurone and distearylether; fatty acids, such as stearic acid, hydroxystearic acid or
5 behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups and mixtures thereof.

The **consistency factors** mainly used are fatty alcohols or
10 hydroxyfatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and also partial glycerides, fatty acids or hydroxyfatty acids. A combination of these substances with alkyl oligoglucosides and/or fatty acid N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates is preferably used. Suitable **thickeners** are, for example,
15 Aerosil types (hydrophilic silicas), polysaccharides, more especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol monoesters and diesters of fatty acids, polyacrylates (for example Carbopols® [Goodrich] or Synthalens® [Sigma]),
20 polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

25 Suitable **cationic polymers** are, for example, cationic cellulose derivatives such as, for example, the quaternized hydroxyethyl cellulose obtainable from Amerchol under the name of Polymer JR 400®, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat®
30 (BASF), condensation products of polyglycols and amines, quaternized

- collagen polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat® L, Grünau), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, amodimethicone, copolymers of adipic acid and dimethylamino-hydroxypropyl diethylenetriamine (Cartaretine®, Sandoz), copolymers of acrylic acid with dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyaminopolyamides as described, for example, in FR 2 252 840 A and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in micro-crystalline distribution, condensation products of dihaloalkyls, for example dibromobutane, with bis-dialkylamines, for example bis-dimethylamino-1,3-propane, cationic guar gum such as, for example, Jaguar®CBS, Jaguar®C-17, Jaguar®C-16 of Celanese, quaternized ammonium salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol.

- Suitable **anionic, zwitterionic, amphoteric and nonionic polymers** are, for example, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and esters thereof, uncrosslinked and polyol-crosslinked polyacrylic acids, acrylamidopropyl trimethylammonium chloride/acrylate copolymers, octylacrylamide/methyl methacrylate/tert.-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, vinyl pyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and optionally derivatized cellulose ethers and silicones.

- Suitable **silicone compounds** are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room

temperature. In addition, a detailed review of suitable liquid silicones was published by Todd et al. in **Cosm. Toil.** 91, 27 (1976).

Typical examples of **fats** are glycerides while suitable **waxes** are inter alia beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax, hydrogenated castor oils, fatty acid esters solid at room temperature or microwaxes, optionally in combination with hydrophilic waxes, for example cetyl stearyl alcohol or partial glycerides. Metal salts of fatty acids such as, for example, magnesium, aluminium and/or zinc stearate or ricinoleate may be used as **stabilizers**.

In the context of the invention, **biogenic agents** are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts, and vitamin complexes.

Suitable **deodorizers** are, for example, antiperspirants, such as aluminium chlorhydrates. These antiperspirants are colorless hygroscopic crystals which readily deliquesce in air and which accumulate when aqueous aluminium chloride solutions are concentrated by evaporation. Aluminium chlorhydrate is used for the production of perspiration-inhibiting and deodorizing compositions and probably acts by partially blocking the sweat glands through the precipitation of proteins and/or polysaccharides [cf. **J. Soc. Cosm. Chem.** 24, 281 (1973)]. For example, an aluminium chlorhydrate which corresponds to the formula $[Al_2(OH)_5Cl] \cdot 2.5H_2O$ and which is particularly preferred for the purposes of the invention is commercially available under the name of Locron® from Hoechst AG of Frankfurt, FRG [cf. **J. Pharm. Pharmacol.** 26, 531 (1975)]. Besides the chlorhydrates, aluminium hydroxylactates and acidic aluminium/zirconium salts may also be used. Other suitable deodorizers are esterase inhibitors, preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and, in particular, triethyl citrate

- (Hydagen® CAT, Henkel KGaA, Düsseldorf, FRG). Esterase inhibitors inhibit enzyme activity and thus reduce odor formation. The free acid is probably released through the cleavage of the citric acid ester, reducing the pH value of the skin to such an extent that the enzymes are inhibited.
- 5 Other esterase inhibitors are sterol sulfates or phosphates, for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfite or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester, hydroxycarboxylic acids and esters thereof, for example
- 10 citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial agents which influence the germ flora and destroy or inhibit the growth of perspiration-decomposing bacteria, may also be present in stick products. Examples of such antibacterial agents are chitosan,
- 15 phenoxyethanol and chlorhexidine gluconate. 5-Chloro-2-(2,4-dichlorophenoxy)-phenol, which is marketed under the name of Irgasan® by Ciba-Geigy of Basel, Switzerland, has also proved to be particularly effective.

- Suitable **antidandruff agents** are climbazol, octopirox and zinc pyrithione. Standard **film formers** are, for example, chitosan,
- 20 microcrystalline chitosan, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds. Suitable **swelling agents** for aqueous phases are
- 25 montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich). Other suitable polymers and swelling agents can be found in R. Lochhead's review in **Cosm. Toil.** 108, 95 (1993).

- Examples of **UV protection factors** include organic substances (light filters) which are liquid or crystalline at room temperature and which
- 30 are capable of absorbing ultraviolet radiation and of releasing the energy

absorbed in the form of longer-wave radiation, for example heat. UV-B filters can be oil-soluble or water-soluble. The following are examples of oil-soluble substances:

- 5 • 3-benzylidene camphor or 3-benzylidene norcamphor and derivatives thereof, for example 3-(4-methylbenzylidene)-camphor, as described in **EP 0693471 B1**;
- 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino)-benzoic acid-2-ethylhexyl ester, 4-(dimethylamino)-benzoic acid-2-octyl ester and 4-(dimethylamino)-benzoic acid amyl ester;
- 10 • esters of cinnamic acid, preferably 4-methoxycinnamic acid-2-ethylhexyl ester, 4-methoxycinnamic acid propyl ester, 4-methoxycinnamic acid isoamyl ester, 2-cyano-3,3-phenylcinnamic acid-2-ethylhexyl ester (Octocrylene);
- 15 • esters of salicylic acid, preferably salicylic acid-2-ethylhexyl ester, salicylic acid-4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- 20 • esters of benzalmalonic acid, preferably 4-methoxybenzalmalonic acid di-2-ethylhexyl ester;
- triazine derivatives such as, for example, 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and Octyl Triazone, as described in **EP 0 818 450 A1**;
- 25 • propane-1,3-diones such as, for example, 1-(4-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione;
- ketotricyclo(5.2.1)decane derivatives, as described in **EP 0 694 521 B1**.

Suitable water-soluble substances are

- 2-phenylbenzimidazole-5-sulfonic acid and alkali metal, alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and salts thereof;
- sulfonic acid derivatives of 3-benzylidene camphor such as, for example, 4-(2-oxo-3-bornylidenemethyl)-benzene sulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)-sulfonic acid and salts thereof.

Typical UV-A filters are, in particular, derivatives of benzoyl methane such as, for example 1-(4'-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione, 4-tert-butyl-4'-methoxydibenzoylmethane (Parsol 1789) or 1-phenyl-3-(4'-isopropylphenyl)-propane-1,3-dione. The UV-A and UV-B filters may of course also be used in the form of mixtures. Besides the soluble substances mentioned, insoluble pigments, i.e. finely dispersed metal oxides or salts, may also be used for this purpose. Examples of suitable metal oxides are, in particular, zinc oxide and titanium dioxide and also oxides of iron, zirconium, silicon, manganese, aluminium and cerium and mixtures thereof. Silicates (talcum), barium sulfate and zinc stearate may be used as salts. The oxides and salts are used in the form of the pigments for skin-care and skin-protecting emulsions and decorative cosmetics. The particles should have an average diameter of less than 100 nm, preferably from 5 to 50 nm and more preferably from 15 to 30 nm. They may be spherical in shape although ellipsoidal particles or other non-spherical particles may also be used. So-called micro- or nanopigments are preferably used in sun protection products. Micronized zinc oxide is preferably used.

Other suitable UV filters can be found in P. Finkel's review in

SÖFW-Journal 122, 543 (1996).

- Besides the two above-mentioned groups of primary protection factors, secondary protection factors of the **antioxidant** type may also be used. Secondary sun protection factors of the antioxidant type interrupt the photochemical reaction chain which is initiated when UV rays penetrate into the skin. Typical examples of suitable antioxidants are amino acids (for example glycine, histidine, tyrosine, tryptophane) and derivatives thereof, imidazoles (for example urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (for example anserine), carotinoids, carotenes (for example α -carotene, β -carotene, lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, liponic acid and derivatives thereof (for example dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (for example thioredoxine, glutathione, cysteine, cystine, cystamine and glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl and glyceryl esters thereof) and their salts, dilaurylthiodipropionate, distearylthiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (for example butionine sulfoximines, homocysteine sulfoximine, butionine sulfones, penta-, hexa- and hepta-thionine sulfoximine) in very small compatible dosages (for example pmole to μ mole/kg), also (metal) chelators (for example α -hydroxyfatty acids, palmitic acid, phytic acid, lactoferrine), α -hydroxy acids (for example citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (for example γ -linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives thereof (for example ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and

derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α -glycosyl rutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiac resin acid, nordihydroguaiaretic acid, trihydroxy-
5 butyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, Superoxid-Dismutase, zinc and derivatives thereof (for example ZnO, ZnSO₄), selenium and derivatives thereof (for example selenium methionine), stilbenes and derivatives thereof (for example stilbene oxide, trans-stilbene oxide) and derivatives of these active substances suitable for
10 the purposes of the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid and the other classes of compounds listed in Appendix 6, Parts A and B of the
15 Kosmetikverordnung ("Cosmetics Directive"). Suitable **insect repellents** are N,N-diethyl-m-toluamide, pentane-1,2-diol or Insect Repellent 3535. A suitable **self-tanning agent** is dihydroxyacetone.

Suitable **perfume oils** are mixtures of natural and synthetic fragrances. Natural fragrances include the extracts of blossoms (lily, lavender, rose, jasmine, neroli, ylang-ylang), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calmus), woods (pinewood, sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage,
20 thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials, for example civet and beaver, may also be used. Typical synthetic perfume compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Examples of perfume compounds
25 of the ester type are benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl
30

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- cyclohexylacetate, linalyl acetate, dimethyl benzyl carbinyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethylmethyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. Ethers include, for example, benzyl ethyl ether while aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal. Examples of suitable ketones are the ionones, α -isomethylionone and methyl cedryl ketone. Suitable alcohols are anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol. The hydrocarbons mainly include the terpenes and balsams. However, it is preferred to use mixtures of different perfume compounds which, together, produce an agreeable fragrance. Other suitable perfume oils are essential oils of relatively low volatility which are mostly used as aroma components. Examples are sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime-blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil. The following are preferably used either individually or in the form of mixtures: bergamot oil, dihydromyrcenol, lilial, lyral, citronellol, phenylethyl alcohol, α -hexylcinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, Boisambrene Forte, Ambroxan, indole, hedione, sandelice, citrus oil, mandarin oil, orange oil, allylamyl glycolate, cyclovertal, lavandin oil, clary oil, β -damascone, geranium oil bourbon, cyclohexyl salicylate, Vertofix Coeur, Iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat.

Suitable **dyes** are any of the substances suitable and approved for cosmetic purposes as listed, for example, in the publication "**Kosmetische Färbemittel**" of the **Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106.**

These dyes are normally used in concentrations of 0.001 to 0.1% by

Typical examples of **germ inhibitors** are preservatives which act specifically against gram-positive bacteria such as, for example, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di-(4-chlorophenyl-biguanido)-hexane) or TCC (3,4,4'-trichlorocarbanilide). Numerous perfumes and essential oils also have antimicrobial properties. Typical examples are the active substances eugenol, menthol and thymol in clove, mint and thyme oil. An interesting natural deodorant is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol) which is present in linden blossom oil and which smells of lily-of-the-valley. Glycerol monolaurate has also been successfully used as a bacteriostatic agent. The percentage content of the additional germ-inhibiting agents is normally about 0.1 to 2% by weight, based on the solids component of the preparations.

The total percentage content of auxiliaries and additives may be from 1 to 50% by weight and is preferably from 5 to 40% by weight, based on the particular composition. The preparations may be produced by standard hot or cold processes and are preferably produced by the phase inversion temperature method.

To produce oil baths, different quantities of various oils were added to the alkanolamide-free surfactant formulation (a):

- (a) 45% by weight of fatty alcohol (polyglycol) ester (alkanolamide-free), 45% by weight of fatty alcohol polyglycol ethers (Dehydol® LS 4 DEO-N, Henkel KGaA) and 10% by weight of polyol (propylene glycol, alkanolamide-free, Henkel KGaA).

and the oil baths obtained were tested for clouding and shelf life at room temperature or 8°C (stable = +). The quantity ratios of surfactant to oil used and the results are set out in Table 1. Oil baths containing surfactant

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Table 1. Oil baths (composition in % by weight)

Composition/performance	Ratio [surfactant:oil]	1 with (a)
Cetiol® A Lauric acid hexyl ester	30:70 50:50	Clear; + Clear; +
Cetiol® OE Dioctyl ether	30:70 50:50	Clear; + Clear; +
Cetiol® PGL Hexyl decanol ester of Guerbet alcohol mixtures	30:70 50:50	Clear; + Clear; +
Eutanol® G Octyl dodecanol ester	30:70 50:50	Clear; + Clear; +
Myritol® 318 Fatty acid triglyceride	30:70 50:50	Clear; + Clear; +
Soya oil	70:30	Clear; +
Sunflower oil	50:50 70:30	Clear; + Clear; +
Castor oil	30:70 50:50	Clear; + Clear; +

[illegible]